

PATENT SPECIFICATION

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(54) MIXTURES OF DISPERSE AZO DYESTUFFS

(71) We, **IMPERIAL CHEMICAL INDUSTRIES LIMITED**, Imperial Chemical House, Millbank, London SW1P 3JF a British Company do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

This invention relates to disperse azo dyestuffs and more particularly to mixtures of two or more disperse monoazo dyestuffs of closely related structure, to a process of manufacture of the said mixtures and to the application of the said mixtures to aromatic polyester textile materials and aromatic polyester/cellulose unions.

According to the present invention there is provided a mixture of two or more monoazo dyestuffs of the formula:



wherein W is chlorine or bromine;

X is hydrogen or OR¹ and

R, R¹, Z and Y are lower alkyl groups;

provided that the mixture contains at least one component in which X is H and one component in which X is OR¹.

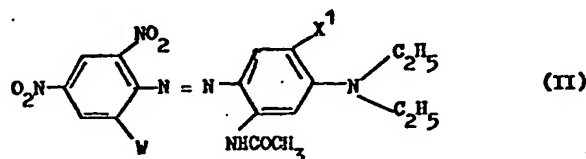
Throughout this specification by "lower alkyl group" we mean an alkyl group containing from 1 to 4 carbon atoms.

As specific examples of lower alkyl groups represented by R, R¹, Y and Z there may be mentioned methyl, ethyl, *n*-propyl, isopropyl, *n*-butyl, *sec*-butyl and isobutyl groups.

In the case in which the mixture of dyestuffs as defined above comprises only two components, then these components may be present in the mixture in a ratio of from 95:5 to 5:95 parts by weight, preferably from 20:80 to 80:20 parts by weight.

When three or more component dyestuffs are present in the mixture, it is preferred that no single dyestuff will comprise less than 5% by weight of the total weight of the mixture.

A preferred mixture of dyestuffs according to the invention is that comprising two dyestuffs having the formula:



in which two dyestuffs W is Br, X' is H and W is Br, X' is methoxy respectively.

Another preferred mixture of dyestuffs according to the invention is that comprising two dyestuffs of formula (II) in which W is Br, X' is H and W is Br, X' is ethoxy, respectively.

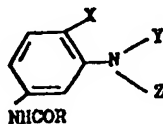
Yet another preferred mixture of dyestuffs according to the invention is that comprising two dyestuffs of formula (II) in which W is Cl, X' is H and W is Cl, X' is methoxy, respectively.

Still another preferred mixture of dyestuffs according to the invention is that comprising two dyestuffs of formula (II) in which W is Cl, X' is H and W is Cl, X' is ethoxy, respectively.

It is further preferred that in each of the above-defined mixtures the dyestuff of formula (II) in which X' is H and the dyestuff of formula (II) in which X' is either methoxy or ethoxy should be in the ratio of from 4:1 to 2:1 by weight, respectively.

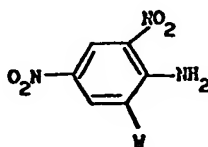
Particularly preferred is a mixture comprising two dyestuffs of formula (II) in which W is Br, X' is H and W is Br, X' is methoxy, in the proportions of approximately 3:1 by weight respectively.

According to a further feature of the invention there is provided a process for the manufacture of the mixtures of disperse monoazo dyestuffs of formula (I) which comprises coupling a mixture of at least two coupling components of formula



(III)

wherein R, X, Y and Z have the meanings stated above, with at least one diazonium compound obtained by diazotisation of an amine of the formula:



(IV)

wherein W has the meaning stated above, provided that the mixture of coupling components contains at least one component in which X is hydrogen and at least one component in which X is OR'.

In the case in which two diazonium compounds are employed in a process as defined above, these may be used by individually diazotising the amines and adding the diazonium compounds so obtained simultaneously or consecutively to the mixture of coupling components, or the amines may be diazotised in admixture and the mixed diazonium compounds so obtained then added to the mixture of coupling components, or the individually prepared diazonium compounds may be mixed together before addition to the mixture of coupling components.

The amine of formula (IV) may be 2,4 - dinitro - 6 - chloroaniline or 2,4 - dinitro - 6 - bromoaniline.

Examples of coupling components of formula (III) are 5 - acetylamino - 2 - methoxy - N,N - diethylaniline, N,N - diethyl - m - aminoacetanilide. The diazotisation and coupling may be carried out by methods conventionally used for these reactions. Thus diazotisation of the amine or amines of formula (IV) may be carried out in nitrosylsulphuric acid in known manner, followed by addition of the resulting solution of the diazo compound to a solution or suspension of the coupling components in water or in a mixture of water and a water-miscible organic liquid, if necessary adjusting the pH of the mixture to facilitate the coupling reaction, and finally isolating the resulting dyestuff by conventional methods.

In addition to preparing mixtures of dyestuffs according to the invention from mixed coupling components and a single diazo component or mixture of diazo components as defined above, such mixtures may of course be obtained by mixing together the individually prepared component dyestuffs of the mixture, obtained by conventional diazotisation and coupling reactions from an amine of formula (IV) and a coupling component of formula (III).

The dyestuff mixtures may be applied to aromatic polyester textile materials by aqueous dyeing, padding or printing methods in the form of aqueous dispersions which are prepared by conventional methods, for example, by milling the dyestuffs with water and a dispersing agent such as the sodium salt of a naphthalene-2-sulphonic acid/formaldehyde condensate, and this colouration process constitutes a further feature of the invention.

The dyestuff mixtures of the present invention provide navy shades on aromatic polyester textile materials which have very good build-up properties and high tinctorial strength superior to the effect achieved by the application of any single component of the dyestuff mixture on its own.

According to a yet further feature of the invention there is provided a process for the colouration of aromatic polyester/cellulose unions which comprises applying to the said unions by an aqueous dyeing, padding or printing process a mixture of two or more disperse monoazo dyestuffs as hereinbefore defined.

It is known that the polyester component of a polyester/cellulose blend can be dyed with disperse dyes, but these dyes suffer from the disadvantage that, particularly when applied by a padding or printing process, they also adhere to the cellulose component. Because disperse dyestuffs have low fastness properties on cellulose materials, that portion of the applied dyestuffs which has stained the cellulose is easily washed off and fades rapidly on exposure to light. Consequently a polyester/cellulose union coloured in this way has poor fastness properties due to loose dye on the cellulose. In order that the coloured union has the maximum fastness properties it is essential that any unfixed dyestuff be removed. This is usually achieved by a "reduction clear" treatment of the coloured union (i.e. a treatment in a warm aqueous alkaline solution of sodium hydrosulphite). However, the disposal of the liquors from the "reduction clear" treatment causes ecological problems due to the presence of the reducing agent. Also a reduction clear treatment cannot be used after the cellulose portion of the blend has been dyed with a dye which is sensitive to this treatment.

Further, in the absence of a "reduction clear" treatment, any dyestuff which is removed by, for example, an ordinary washing treatment can give rise, especially in the case of printing, to back staining resulting in the staining of other areas of the print, or dull tones.

The above described problems are minimized by the use of mixtures of disperse monoazo dyestuffs as hereinbefore defined, which cause a minimum of staining of the cellulose portion of the blend.

The process may be carried out by immersing the polyester/cellulose union in a dyebath comprising an aqueous dispersion of the two or more monoazo dyestuffs as defined above, which dyebath preferably contains a non-ionic, cationic and/or anionic surface-active agent, and thereafter heating the dyebath for a period at a suitable temperature. The dyeing process may either be carried out at a temperature between 95 and 100°C, preferably in the presence of a carrier such as diphenyl, *o*-hydroxydiphenyl, methyl naphthalene, methyl salicylate or trichlorobenzene, or at a temperature from 120°C to 140°C, under superatmospheric pressure.

The process of the invention may also be carried out by padding on to the polyester/cellulose union an aqueous dispersion of two or more disperse monoazo dyestuffs as hereinbefore defined, the dyestuffs then being fixed on the union by steaming said union for short periods at a temperature between 100 and 180°C or baking at temperatures between 160° and 220°C. If desired the padding liquor can contain the conventional additives, for example, dispersing agents, thickeners, migration inhibitors or urea.

As a further method of application a thickened printing paste containing two or more disperse monoazo dyestuffs in dispersed form may be applied to the surface of the polyester/cellulose union by any of the methods conventionally used for applying printing pastes to textile materials, for example by block, screen or roller printing. The printed textile material, optionally after being dried, is then steamed for short periods at temperatures between 100° and 180°C, or is baked at temperatures between 160°C and 220°C. Suitable thickening agents which are present in the printing paste include gum tragacanth, gum arabic, alginates, for example, sodium or ammonium alginates, oil-in-water or water-in-oil emulsions, or thickening agents of synthetic origin based on ethylene/maleic anhydride copolymers or polyacrylic acids. The printing pastes can also contain conventional additives such as urea, sodium *m*-nitrobenzene sulphonate, diimides, acids or alkalis to assist in bringing about fixation of the various dyestuffs.

After the dyeing, padding or printing process has been carried out, the coloured textile material is then rinsed in water.

The aromatic polyester/cellulose unions used in the process of the invention can be any textile materials which are mixtures of aromatic polyester fibres and cellulose fibres. Such unions are usually in the form of knitted, or preferably woven goods. The percentage of aromatic polyester fibres may be in the range of 20 to 95%, generally 30 to 85%, by weight of the weight of the union. The aromatic polyester fibres are preferably polyethylene terephthalate fibres and the cellulose fibres are preferably cotton, linen, viscose rayon or polynosic rayon fibres.

By the use of mixtures of disperse monoazo dyestuffs as hereinbefore defined in the process of the invention the aromatic polyester part of the polyester/cellulose union is coloured in navy shades with excellent reserve of the cellulose part of the union, i.e. the cellulose remains uncoloured or virtually so. Any staining of the cellulose which does occur can be removed by a "reduction clear" treatment which is very much milder than that conventionally employed, with a corresponding reduction in the different disposal problem.

The process of the present invention can also be applied to the colouration of unions containing aromatic polyester and cellulose whereby the mixture of disperse monoazo dyestuffs as hereinbefore defined is applied in conjunction with one or more colouring matters for the cellulose component of the union, and this constitutes a still further feature of the invention.

Examples of colouring matters for the cellulose part of the polyester/cellulose unions are direct dyestuffs, vat dyestuffs, sulphur dyestuffs, azoic colouring matters, or reactive dyestuffs.

The mixture of disperse monoazo dyestuffs for the aromatic polyester part of the union and a colouring matter from one of the above-defined classes for the cellulose part of the union may in general be applied concurrently or consecutively, by the conventional processes.

Though the dyes employed in this invention may be applied to a polyester/cellulose blend by all conventional processes and together with all classes of dyes for cellulose, a particular advantage of these dyes is that since they have good cellulose reserve and dyeings of high fastness can be obtained using processes which do not involve a reduction clearing treatment. This permits the use of simple and economical processes, as exemplified below.

Thus, the polyester/cellulose material may be padded with a liquor containing disperse and reactive dyes, dried, baked or steamed at high temperature to fix the disperse dyes on the polyester component, padded in aqueous alkali, steamed to fix the reactive dye on the cellulose component, washed and dried.

Alternatively, the pad liquor can contain alkali, and fixation of the reactive dye be achieved during drying prior to baking, thus avoiding the need for an alkali pad-steam treatment.

In batchwise processing the polyester component can be dyed in any conventional manner, the dyeing given a mild reduction clearing treatment, or no treatment at all, the cellulose portion then being dyed by any process, using any class of dye for cellulose.

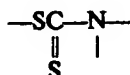
The cellulose portion can first be dyed with reactive dye, the material rinsed until neutral, and the polyester component then dyed with the mixture of disperse dyes in a separate dyebath either under pressure or with a carrier, washed and dried. Or the cellulose can be dyed first with a reactive dye, after which the mixture of disperse dyes is added to the exhausted dyebath, the pH adjusted and any auxiliary products added, and the polyester component dyed either at the boil with a carrier, or under pressure.

The reactive dyestuffs used in the process of the invention may be any water-soluble dyestuffs which contain at least one fibre-reactive group, this being defined as a group whose presence in the dyestuff molecule renders the dyestuff capable of chemically combining with hydroxy groups present in cellulose textile materials so that the dyestuff molecule becomes attached to the cellulose molecule through a covalent chemical bond or bonds. Each fibre-reactive group is attached to a carbon atom present in the dyestuff molecule and preferably to a carbon atom of an aromatic ring, preferably a benzene ring, present in the dyestuff molecule. The said dyestuffs are preferably dyestuffs of the azo, including monoazo and polyazo and metallised azo dyes, anthraquinone, formazan, triphenyloxazine, nitro and phthalocyanine series containing at least one fibre-reactive group.

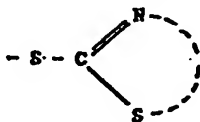
As examples of fibre-reactive groups there may be mentioned acylamino radicals derived from olefinically unsaturated aliphatic carboxylic acids such as

acryloylamino and crotonylamino, or from halogen-substituted aliphatic carboxylic acids such as β -chloropropionylamino, β -bromopropionylamino, β , γ , γ -trichlorocrotonylamino and tetrafluorocyclobutylacryloylamino. Alternatively the fibre-reactive group can be a vinyl sulphone, β -chloroethyl sulphone, β -sulphatoethylsulphonyl, β -chloroethylsulphonamide or an optionally N-substituted β -aminoethylsulphonyl group.

The fibre-reactive group is preferably a heterocyclic radical having two or three nitrogen atoms in the heterocyclic ring and at least one labile substituent attached to a carbon atom of the heterocyclic ring. By "labile substituent" is meant a substituent which is displaced from the fibre-reactive group in the formation of a covalent bond between the fibre-reactive group and cellulose. As examples of labile substituents there may be mentioned chlorine, bromine, fluorine, quaternary ammonium groups, thiocyanato, sulphonic acid, hydrocarbonylsulphonyl groups, groups of the formula



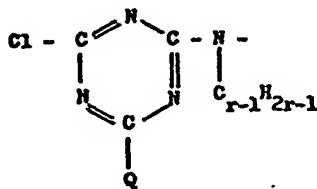
wherein the nitrogen atom carries optionally substituted hydrocarbon or heterocyclic radicals, and groups of the formula:—



wherein the dotted line indicates the atoms necessary to form an optionally substituted or fused heterocyclic ring. Preferably the reactive dyestuff carries a triazine or pyrimidine ring containing as the labile substituent at least one chlorine, bromine or fluorine atom.

As specific examples of such fibre-reactive heterocyclic radicals there may be mentioned 3,6 - dichloropyridazine - 4 - carbonylamino, 2,3 - dichloroquinoxaline - 5 - or 6 - (sulphonyl or carbonyl) amino, 2,4 - dichloroquinazoline - 6- or 7 - sulphonylamino, 2,4,6 - trichloroquinazoline - 7- or 8 - sulphonylamino, 2,4,7- or 2,4,8 - trichloroquinazoline - 6 - sulphonylamino, 2,4 - dichloroquinazoline - 6 - carbonylamino, 1,4 - dichlorophthalazine - 6 - carbonylamino, 4,5 - dichloropyridazon - 1 - yl amino, 2,4 - dichloropyrimidin - 5 - yl carbonylamino, 1 - (phenyl - 4' - carbonylamino) - 4,5 - dichloropyridazone, 2,4- and/or 2,6 - dichloro- or bromo - pyridin - 6 - (and/or 4)yl amino, difluorochloropyrimidinyl amino, trichloropyrimidinyl amino, tribromopyrimidinyl amino, dichloro - 5 - (cyano, nitro, methyl or carbomethoxy)pyrimidinyl amino, 2 - methylsulphonyl - 6 - chloropyrimidin - 4 - yl carbonylamino and 5 - chloro - 6 - methyl - 2 - methylsulphonylpyrimidin - 4 - yl amino, and more particularly 1,3,5 - triazin - 2 - yl amino radicals which contain a fluorine or a bromine and, especially a chlorine atom on at least one of the 4- and 6- positions, for example 4,6 - dichloro - 1,3,5 - triazin - 2 - yl amino. When the triazine nucleus contains only a single halogen atom, preferably a chlorine atom, then the third carbon atom of the triazine ring may be substituted by a hydrocarbon radical, such as methyl or phenyl, but more particularly by an optionally substituted hydroxy, mercapto or amino group, such as methoxy, phenoxy, α - and β -naphthoxy, methylmercapto, phenylthio, methylamino, diethylamino, cyclohexylamino and anilino and N-alkylanilino and substituted derivatives thereof such as anisidino, toluidino, carboxyl-anilino, sulphoanilino, disulphoanilino and sulphonated naphthylamino.

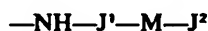
Thus a preferred class of the reactive dyestuffs comprises those dyestuffs which contain as the fibre-reactive group a group of the formula:



wherein r is 1 or 2, and Q is a chlorine atom, an optionally substituted amino group or an etherified hydroxyl group.

The optionally substituted amino groups represented by Q are preferably optionally substituted alkylamino, anilino, or N -alkylanilino groups, e.g. methylamino, ethylamino, β -hydroxyethylamino, di(β -hydroxyethyl)amino, β -methoxyethylamino, β -sulphatoethylamino, o -, m - and p -sulphoanilino, 4- and 5-sulpho-2-carboxyanilino, 4- and 5-sulpho-2-methoxyanilino, 4- and 5-sulpho-2-methylanilino, 4- and 5-sulpho-2-chloroanilino, 4- and 5-sulpho-2-chloroanilino, 2,4-, 2,5- and 3,5-disulphoanilino, N -methyl- m - and p -sulphoanilino.

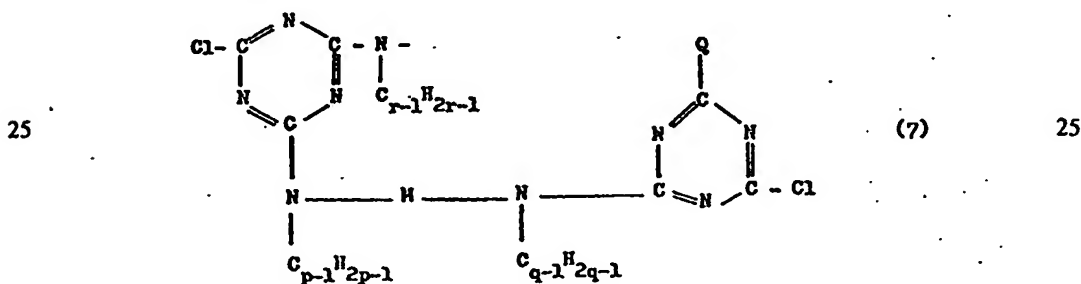
If desired the fibre-reactive group may be of the type:



wherein J^1 is a pyrimidine or triazine ring optionally carrying a labile substituent, J^2 is a pyrimidine or triazine ring carrying at least one labile substituent and M is a bridging member which is linked to J^1 and J^2 through optionally substituted imino groups, said imino groups being linked together through an alkylene or arylene radical such as ethylene, 1,4-phenylene or 2-sulpho-1,4-phenylene.

Other linking groups of particular interest represented by M are the divalent radicals of stilbene, diphenyl, diphenyloxide, diphenylamine, diphenylurea, diphenoxyethane and diphenylamino- s -triazine, which contain a sulphonic acid group in each benzene nucleus.

It is preferred that J^1 and J^2 should each represent a chloro- s -triazine group. Thus, a further class of reactive dyestuffs comprises those dyestuffs which contain as the fibre-reactive group a group of the formula:



wherein r , p and q are each independently 1 or 2, and M and Q have the meanings stated above.

The group Q , as previously defined, includes within its scope groups which contain a chromophoric system linked to the carbon atom of the triazine ring through $-\text{NH}-$ or $-\text{O}-$.

Such reactive dyestuffs can be obtained in conventional manner, for example, by reacting a water-soluble dyestuff containing a primary or secondary amino group with a compound which contains the said fibre-reactive group. As examples of such compounds there may be mentioned acryloyl chloride, cyanuric chloride, 2,4,6-trichloropyrimidine, 2,4,6-trichloro-5-(cyano- or chloro-)pyrimidine and 6-methoxy-2,4-dichloro-1,3,5-triazine.

Other preferred reactive dyestuffs are those containing one or more phosphorous acid groups, particularly phosphonic acid groups, which are applied to cellulose textile materials by the methods described in U.K. Patent Specification No. 1411306.

By this process of the invention aromatic polyester/cellulose unions are coloured in a variety of shades which have excellent fastness to the tests commonly applied to such textile materials, and there is excellent reserve of the white unprinted portions of such textile materials.

The preparation of certain coupling components and dyestuffs for the particularly preferred mixtures according to the present invention is described below. Parts are by weight unless otherwise indicated, the ratio of parts by weight to parts by volume being that of the kilogram to the litre.

Preparation of 5 - acetylamino - 2 - methoxy - N,N - diethylaniline

18 parts of 5 - acetylamino - 2 - methoxyaniline are stirred in 50 parts by volume of water. Aqueous sodium hydroxide solution (70° Tw) is added to adjust the pH to 9—10. The mixture is heated to 65°C and a dispersing agent (polyglycerolricinoleate, 0.5 part) is added followed by 29.4 parts of sodium bicarbonate (equivalent to 3.5 moles per mole of the aniline starting material). 54 parts of diethylsulphate (3.5 moles per mole of starting material) is then added over a period of 2 hours at 65°C. Reaction proceeded smoothly. Stirring of the mixture at 65°C was continued for a further 2 hours after addition of the diethylsulphate to complete the reaction. The reaction mixture was cooled to room temperature and the 5 - acetylamino - 2 - methoxy - N,N - diethylaniline was collected, washed with water (500 parts by volume) and dried at 70°C. *N,N* - Diethyl - *m* - aminoacetanilide is prepared in similar manner starting from *m*-aminoacetanilide.

Preparation of the dyestuff of formula (II) in which X' is methoxy

70 parts (by volume) of 100% sulphuric acid are added to 4 parts of water. 7 parts of sodium nitrite are then added portionwise to the stirred acid at a rate such as to raise the temperature of the mixture to 70±2°C and to maintain it at that level. On completion of the addition of sodium nitrite the solution is stirred for 1 hour, the temperature being allowed to fall to room temperature. 26.2 parts of 2,4 - dinitro - 6 - bromoaniline are added to the stirred sodium nitrite solution at 25—28°C during 30 minutes. On completion of the addition the solution is stirred for 2 hours at room temperature.

23.6 parts of 5 - acetylamino - 2 - methoxy - N,N - diethylaniline are stirred in 500 parts of water and 10 parts by volume of concentrated hydrochloric acid are added. Ice is added to the solution to lower the temperature to 0°C and anhydrous sodium acetate is added to adjust the pH to 3—4. The diazotised amine solution is then added dropwise during 30 minutes at 0°C and pH4 (controlled by the addition of ice and sodium acetate) until only a trace of excess coupling component remains as shown by testing the mixture with diazotised *p*-nitroaniline. The mixture is stirred for a further 15 minutes at 0—5°C, and the dyestuff is collected and washed free from inorganic contaminants with water. The dyestuff is dissolved in boiling acetone, the solution is filtered and the dyestuff is re-precipitated by the addition of ice and water to the acetone solution. The product is again collected washed with water and dried at 70°C.

Preparation of the dyestuff of formula (II) in which X' is hydrogen

2,4 - Dinitro - 6 - bromoaniline (26.2 parts) is diazotised and coupled with 20.6 parts of N,N - diethyl - *m* - aminoacetanilide exactly as described for the preceding preparation.

The invention is illustrated but not limited by the following Examples in which parts and percentages are by weight.

Example 1

10 Parts of the dyestuffs in formula (II) in which W is Br, X' is methoxy and W is Br, X' is hydrogen respectively are individually gravel milled with 12.8 parts of an aqueous solution of a dispersing agent (sodium salt of a naphthalene - 2 - sulphonic acid/formaldehyde condensate), containing 39.2% by weight of the agent, and 77.2 parts of water. After 48 hours milling the particle size of each dyestuff in its dispersion is 3—4 microns.

0.3 part of the 10% aqueous dispersion of the dyestuff of formula (II) in which W is Br, X' is hydrogen, and 0.075 part of the 10% aqueous dispersion of the dyestuff of formula (II) in which W is Br, X' is methoxy, both dispersions being obtained as described above, are transferred into a dyeing vessel. 0.5 part by volume of a buffer solution is added, followed by 5 parts of aromatic polyester piece textile material. The dyebath is then made up to 50 parts with water and dyeing is effected under superatmospheric pressure at 130°C for 1 hour.

On completion of dyeing the dyed material is stirred in a reduction clearing bath comprising 5 parts of sodium hydrosulphite, 3 parts by volume of sodium hydroxide solution (70° Tw), 3 parts by volume of a dispersing agent and 490 parts by volume of water, for 30 minutes at 70°C. The fibre is then thoroughly washed in a soap solution, rinsed well in water and dried.

The polyester is dyed in a navy blue shade having very good build up and high tinctorial strength.

Example 2

The dyeing procedure described in Example 1 is repeated except that the 10% aqueous dispersion of the dyestuff of formula (II) in which W is Br, X' is H and the 10% aqueous dispersion of the dyestuff of formula (II) in which W is Br, X' is methoxy are used in the following amounts:—

	(II) W is Br, X' is H	(II) W is Br, X' is methoxy
(a)	0.10	0.30
(b)	0.20	0.20
(c)	0.25	0.15
(d)	0.30	0.10
(e)	0.35	0.05

In each case a strong navy blue shade on polyester textile material is obtained.

Example 3

The dyeing procedure described in Example 1 is repeated except that the 0.075 part of the 10% aqueous dispersion of the dyestuff of formula (II) in which W is Br, X' is methoxy is replaced by 0.1 part of a 10% aqueous dispersion of one of the following dyestuffs of formula (I). W, X, Y, Z and R in the table below have the same significance as in formula (I).

	W	X	Y	Z	R
(a)	Br	OCH ₃	CH ₃	CH ₃	CH ₃
(b)	Br	OCH ₃	C ₂ H ₅ (n)	C ₂ H ₅ (n)	CH ₃
(c)	Br	OC ₂ H ₅ (n)	C ₂ H ₅	C ₂ H ₅	CH ₃
(d)	Br	OCH ₃	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅
(e)	Cl	OCH ₃	C ₂ H ₅	C ₂ H ₅	CH ₃
(f)	Br	OC ₂ H ₅	C ₂ H ₅	C ₂ H ₅	CH ₃
(g)	Br	OC ₂ H ₅ (n)	C ₂ H ₅	C ₂ H ₅	CH ₃
(h)	Br	OCH ₃	C ₄ H ₉ (n)	C ₄ H ₉ (n)	CH ₃
(i)	Br	OCH ₃	CH ₃	C ₄ H ₉ (n)	CH ₃
(j)	Br	OCH ₃	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅ (n)
(k)	Br	OCH ₃	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅ (iso)

Each dyestuff mixture when applied to aromatic polyester textile material as described in Example 1 gives a strong navy blue shade.

Example 4

The dyeing procedure described in Example 1 is repeated except that the 0.075 part of the 10% aqueous dispersion of the dyestuff of formula (II) in which W is Br, X' is methoxy is replaced by 0.1 part of the same dyestuff dispersion, and the 0.3 part of the 10% aqueous dispersion of the formula (II) in which W is Br, X' is hydrogen is replaced by 0.3 part of a 10% aqueous dispersion of one of the following dyestuffs of formula (I). W, X, Y, Z and R in the table below have the same significance as in formula (I).

	W	X	Y	Z	R
(a)	Br	H	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅
(b)	Cl	H	C ₂ H ₅	C ₂ H ₅	CH ₃
(c)	Br	H	CH ₃	CH ₃	CH ₃
(d)	Br	H	C ₂ H ₅ (n)	C ₂ H ₅ (n)	CH ₃
(e)	Br	H	C ₄ H ₉ (n)	C ₄ H ₉ (n)	CH ₃
(f)	Br	H	CH ₃	CH ₂ CH(CH ₃) ₂	CH ₃
(g)	Br	H	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅ (n)

Each dyestuff mixture when applied to aromatic polyester textile material as described in Example 1 gives a strong navy blue shade.

Example 5

0.3 part of a 10% aqueous dispersion of the dyestuff of formula (II) in which W is Br, X' is hydrogen, 0.05 part of a 10% aqueous dispersion of the dyestuff of formula (II) in which W is Br, X' is methoxy and 0.05 part of a 10% aqueous dispersion of the dyestuff of formula (II) in which W is Br, X' is ethoxy are mixed

together. This mixture when applied to aromatic polyester textile material by the method described in Example 1 gives strong navy blue shades.

Similar results are obtained if the dyestuff of formula (II) in which W is Br, X' is ethoxy is replaced by the dyestuff of formula (I) in which W is bromine, X is methoxy Y and Z are each *n*-propyl and R is methyl.

Example 6

A mixture is made in the proportions given below, of the 10% aqueous dispersions of four dyestuffs of formula (I) in which Y and Z are each ethyl, R is methyl and W and X have the meanings given below.

W	X	
Br	H	1.5 part
Cl	H	1.5 part
Br	OCH ₃	0.5 part
Cl	OCH ₃	0.5 part

This mixture when applied to aromatic polyester textile material by the method described in Example 1 gives strong navy blue shades.

Example 7

26.2 Parts of 2,4 - dinitro - 6 - bromoaniline are diazotised by the method described previously and the diazonium compound so obtained is coupled with a mixture of 6.0 parts of 5 - acetyl amino - 2 - methoxy - N,N - diethylaniline and 15.4 parts of N,N - diethyl - *m* - aminoacetanilide by the method described previously. The mixed dyestuff so obtained when applied in the form of an aqueous dispersion to aromatic polyester textile material as described in Example 1 gives strong navy blue shades.

Example 8

The dyeing procedure described in Example 1 is repeated except that the 0.3 part of a 10% aqueous dispersion of the dyestuff of formula (II) in which W is Br, X' is hydrogen is replaced by 0.3 part of a 10% aqueous dispersion of the dyestuff of formula (II) in which W is Cl, X' is hydrogen, and the 0.075 part of the 10% aqueous dispersion of the dyestuff of formula (II) in which W is Br, X' is methoxy is replaced by 0.1 part of a 10% aqueous dispersion of one of the following dyestuffs of formula (I). W, X, Y, Z and R in the table below have the same significance as in formula (I).

	W	X	Y	Z	R
(a)	Cl	OCH ₃	C ₂ H ₅	C ₂ H ₅	CH ₃
(b)	Cl	OC ₂ H ₅	C ₂ H ₅	C ₂ H ₅	CH ₃
(c)	Cl	OCH ₃	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅
(d)	Cl	OCH ₃	C ₃ H ₇ (<i>n</i>)	C ₃ H ₇ (<i>n</i>)	CH ₃

Each dyestuff mixture when applied to aromatic polyester textile material as described in Example 1 gives a strong navy blue shade.

Example 9

A 67/33 woven blend of aromatic polyester/cotton fibres is padded in a padding liquor of the following constitution, so that the material retains 50% of its weight of the padding liquor.

1 part of the dyestuff of formula (II) in which W is Br, X' is hydrogen, as a 10% aqueous dispersion,

4 parts of the dyestuff of formula (II) in which W is Br, X' is methoxy, as a 10% aqueous dispersion,

10 parts urea,

10 parts Matexil FA—MIV (a migration inhibitor marketed by Imperial Chemical Industries Limited; "Matexil" is a Registered Trade Mark) .

10 parts sodium bicarbonate per 1000 parts of pad liquor.

The dyes are preferably in the form of an aqueous dispersion, milled in the presence of an equal weight of a protective agent such as sodium salt of a naphthalene-2-sulphonic acid/formaldehyde condensate.

The padded material is dried for 30 seconds at 110°C, baked for 60 seconds at 210°C, rinsed in hot water, treated for 30 seconds at 80°C in a solution containing

2g/litre Synperonic BD (a synthetic detergent marketed by Imperial Chemical Industries Limited; "Synperonic" is a Registered Trade Mark) rinsed in cold water and dried. The above series of operations can conveniently be carried out as a continuous sequence.

5 The polyester portion of the blend is dyed to a full, reddish navy shade while the cotton portion is only slightly stained, and the fabric has good fastness to light and washing. 5

Example 10

10 The padding procedure described in Example 9 is repeated except that the dyestuff of formula (II) in which W is Br, X' is hydrogen and the dyestuff of formula (II) in which W is Br, X' is methoxy are used in the following proportions:— 10

	(II) W is Br, X' is H	(II) W is Br, X' is methoxy	
15	(a) 1.0	3.0	
	(b) 2.0	2.0	15
	(c) 2.5	1.5	
	(d) 3.0	1.0	
	(e) 3.5	0.5	

In each case a similar result to that described in Example 9 is obtained.

Example 11

20 The padding procedure described in Example 9 is repeated except that the 1 part of the dyestuff of formula (II) in which W is Br, X' is hydrogen is increased to 3 parts, and the 4 parts of the dyestuff of formula (II) in which W is Br, X' is methoxy are replaced by 1 part of one of the following dyestuffs of formula (I). W, X, Y, Z and R in the table below have the same significance as in formula (I). 20

	W	X	Y	Z	R	
30	(a) Br	OCH ₃	CH ₃	CH ₃	CH ₃	
	(b) Br	OCH ₃	C ₂ H ₅ (n)	C ₂ H ₅ (n)	CH ₃	
	(c) Br	OC ₂ H ₅ (n)	C ₂ H ₅	C ₂ H ₅	CH ₃	30
	(d) Br	OCH ₃	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅	
	(e) Cl	OCH ₃	C ₂ H ₅	C ₂ H ₅	CH ₃	
	(f) Br	OC ₂ H ₅	C ₂ H ₅	C ₂ H ₅	CH ₃	
	(g) Br	OC ₂ H ₅ (n)	C ₂ H ₅	C ₂ H ₅	CH ₃	
35	(h) Br	OCH ₃	C ₂ H ₅ (n)	C ₂ H ₅ (n)	CH ₃	
	(i) Br	OCH ₃	CH ₃	C ₂ H ₅ (n)	CH ₃	35
	(j) Br	OCH ₃	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅ (n)	
	(k) Br	OCH ₃	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅ (iso)	

In each case a similar result to that described in Example 9 is obtained.

Example 12

40 The padding procedure described in Example 9 is repeated except that 4 parts of the dyestuff of formula (II) in which W is Br, X' is methoxy are reduced to 1 part, and the 1 part of the dyestuff of formula (II) in which W is Br, X' is hydrogen is replaced by 3 parts of one of the following dyestuffs of formula (I). W, X, Y, Z and R in the table below have the same significance as in formula (I). 40

	W	X	Y	Z	R	
45	(a) Br	H	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅	
	(b) Cl	H	C ₂ H ₅	C ₂ H ₅	CH ₃	
	(c) Br	H	CH ₃	CH ₃	CH ₃	
	(d) Br	H	C ₂ H ₅ (n)	C ₂ H ₅ (n)	CH ₃	
50	(e) Br	H	C ₂ H ₅ (n)	C ₂ H ₅ (n)	CH ₃	50
	(f) Br	H	CH ₃	CH ₂ CH(CH ₃) ₂	CH ₃	
	(g) Br	H	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅ (n)	

In each case a similar result to that described in Example 9 is obtained.

Example 13

55 The padding procedure described in Example 9 is repeated except that the 1 part of the dyestuff of formula (II) in which W is Br, X' is hydrogen and the 4 parts 55

of the dyestuff of formula (II) in which W is Br, X' is methoxy are replaced by 3 parts of the dyestuff of formula (II) in which W is Br, X' is hydrogen, 0.5 part of the dyestuff of formula (II) in which W is Br, X' is methoxy and 0.5 part of the dyestuff of formula (II) in which W is Br, X' is ethoxy.

5 A similar result to that described in Example 9 is obtained.

If the dyestuff of formula (II) in which W is Br, X' is ethoxy is replaced by the same amount of the dyestuff of formula (I) in which W is bromine, R is methyl, X is methoxy, and Y and Z are each *n*-propyl, a similar result is obtained.

Example 14

10 The padding procedure described in Example 9 is repeated except that the 1 part of the dyestuff of formula (II) in which W is Br, X' is hydrogen and the 4 parts of the dyestuff of formula (II) in which W is Br, X' is methoxy are replaced, in the proportions given below, by four dyestuffs of formula (I) in which Y and Z are each ethyl, R is methyl and W and X have the meanings given below:—

W	X	
Br	H	1.5 parts
Cl	H	1.5 parts
Br	OCH ₃	0.5 parts
Cl	OCH ₃	0.5 parts

15 A similar result to that described in Example 9 is obtained.

Example 15

A mixture of dyestuffs of formula (II) in which W is Br, X' is hydrogen and W is Br, X' is methoxy respectively is prepared as described in Example 7 and converted into a 10% aqueous dispersion.

25 When this dispersion is applied to an aromatic polyester/cotton blend as described in Example 9 a similar result is obtained.

Example 16

30 The padding procedure described in Example 9 is repeated except that the 1 part of the dyestuff of formula (II) in which W is Br, X' is hydrogen and the 4 parts of the dyestuff of formula (II) in which W is Br, X' is methoxy are replaced by 3 parts of the dyestuff of formula (II) in which W is Cl, X' is hydrogen and 1 part of one of the following dyestuffs of formula (I) respectively. W, X, Y, Z and R in the table below have the same significance as in formula (I).

	W	X	Y	Z	R
35 (a)	Cl	OCH ₃	C ₂ H ₅	C ₂ H ₅	CH ₃
(b)	Cl	OC ₂ H ₅	C ₂ H ₅	C ₂ H ₅	CH ₃
(c)	Cl	OCH ₃	C ₂ H ₅	C ₂ H ₅	C ₂ H ₅
(d)	Cl	OCH ₃	C ₃ H ₇ (<i>n</i>)	C ₃ H ₇ (<i>n</i>)	CH ₃

In each case a result similar to that described in Example 9 is obtained.

40 WHAT WE CLAIM IS:—

1. A mixture of two or more disperse monoazo dyestuffs of the formula:



wherein W is chlorine or bromine;

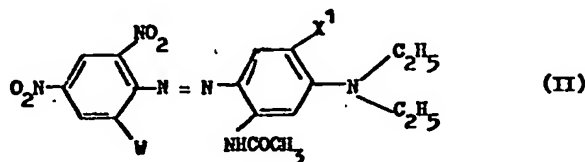
X is hydrogen or OR' and

45 R, R', Y and Z are lower alkyl groups, as hereinbefore defined provided that the mixture contains at least one component in which X is H and one component in which X is OR'.

2. A dyestuff as claimed in claim 1 which comprises two components in a ratio of from 95:5 to 5:95 parts by weight.

3. A dyestuff mixture as claimed in claim 2 which comprises the two components in a ratio of from 80:20 to 20:80 parts by weight.

4. A dyestuff as claimed in claim 1 which comprises two dyestuffs having the formula:



in which W is Br, X' is H and W is Br, X' is methoxy, respectively.

5. A dyestuff mixture as claimed in claim 4 wherein the dyestuff in which W is Br, X' is H and the dyestuff in which W is Br, X' is methoxy are in the ratio of from 4:1 to 2:1 by weight, respectively.

6. A dyestuff mixture of formula (II) as defined in claim 4 in which W is Br, X' is H and W is Br, X' is ethoxy, respectively.

7. A dyestuff mixture of formula (II) defined in claim 4 in which W is Cl, X' is H and W is Cl, X' is methoxy, respectively.

8. A dyestuff mixture of formula (II) as defined in claim 4 in which W is Cl, X' is H and W is Cl, X' is ethoxy, respectively.

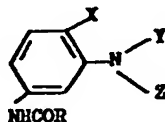
9. A dyestuff mixture as claimed in any one of claims 6 to 8 wherein the dyestuff in which X' is H and the dyestuff in which X' is methoxy or ethoxy are in the ratio of from 4:1 to 2:1 by weight, respectively.

10. A dyestuff mixture as claimed in claim 5 wherein the dyestuff in which W is Br, X' is H and the dyestuff in which W is Br, X' is methoxy are in the proportions of approximately 3:1 by weight, respectively.

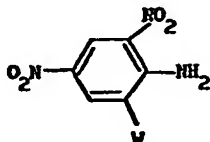
11. A mixture of two or more disperse monoazo dyestuffs substantially as hereinbefore described in the foregoing Example 1 or Example 9.

12. A mixture of two or more disperse monoazo dyestuffs substantially as hereinbefore described in any one of the foregoing Examples 2 to 8 and 10 to 16.

13. A process for the manufacture of the mixtures of disperse monoazo dyestuffs claimed in claim 1 which comprises coupling a mixture of at least two coupling components of formula:



wherein R, X, Y and Z are as defined in claim 1, with at least one diazonium compound obtained by diazotisation of an amine of formula:



wherein W is as defined in claim 1, provided that the mixture of coupling components contains at least one component in which X is hydrogen and at least one component in which X is OR'.

14. A process as claimed in claim 13 substantially as hereinbefore described in the foregoing Example 7.

15. Mixtures of disperse monoazo dyestuffs whenever obtained by a process as claimed in claim 13 or claim 14.

16. A process for the colouration of aromatic polyester textile materials which comprises applying to the aromatic polyester textile material by an aqueous dyeing, padding or printing process a mixture of disperse monoazo dyestuffs as claimed in claim 1.

17. A process for the colouration of aromatic polyester textile materials substantially as hereinbefore described in the foregoing Example 1.

18. A process for the colouration of aromatic polyester textile materials substantially as hereinbefore described in any one of the foregoing Examples 2 to 8.

5 19. Aromatic polyester textile material whenever coloured by a process as claimed in claim 16 or claim 17. 5

20. Aromatic polyester textile material whenever coloured by a process as claimed in claim 18.

10 21. A process for the colouration of aromatic polyester/cellulose unions which comprises applying to the said union by an aqueous dyeing, padding or printing process a mixture of two or more disperse monoazo dyestuffs as claimed in claim 1. 10

22. A process for the colouration of aromatic polyester/cellulose unions substantially as hereinbefore described in the foregoing Example 9.

15 23. A process for the colouration of aromatic polyester/cellulose unions substantially as hereinbefore described in any one of the foregoing Examples 10 to 16. 15

24. Aromatic polyester/cellulose unions whenever coloured by a process as claimed in claim 21 or claim 22.

20 25. Aromatic polyester/cellulose unions whenever coloured by a process as claimed in claim 23. 20

26. A process as claimed in claim 21 wherein the mixture of two or more disperse monoazo dyestuffs is applied in conjunction with one or more colouring matters for the cellulose component of the union.

25 27. A process as claimed in claim 26 wherein the colouring matter for the cellulose component of the union is a direct dyestuff, vat dyestuff, sulphur dyestuff, azoic colouring matter or reactive dyestuff. 25

28. A process as claimed in claim 27 wherein the colouring matter for the cellulose component of the union is a reactive dyestuff which contains as the fibre-reactive group (as hereinbefore defined) a heterocyclic radical having two or three nitrogen atoms in the heterocyclic ring and at least one labile substituent as hereinbefore defined to a carbon atom of the heterocyclic ring. 30

29. A process as claimed in claim 28 wherein the reactive dyestuff contains a triazine or pyrimidine ring containing as the labile substituent at least one chlorine, bromine or fluorine atom.

35 30. Aromatic polyester/cellulose unions whenever coloured by a process as claimed in any one of claims 26 to 29. 35

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